Novel self assembled monolayers of allyl phenyl thiophene ether as potential dielectric material for organic thin film transistors

A. Sathyapalan\textsuperscript{a,b}, S.C. Ng\textsuperscript{b,*}, A. Lohani\textsuperscript{a}, T.T. Ong\textsuperscript{b}, H. Chen\textsuperscript{b}, S. Zhang\textsuperscript{c}, Y.M. Lam\textsuperscript{a}, S.G. Mhaisalkar\textsuperscript{a}

\textsuperscript{a} School of Materials Science and Engineering, Nanyang Technological University, Singapore
\textsuperscript{b} School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore
\textsuperscript{c} School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

Available online 14 July 2007

Abstract

Allyl phenyl thiophene ether as novel potential dielectric materials for organic thin film transistors have been synthesized by coupling 2-bromothiophene with 4-bromo allyl phenyl ether and was systematically characterized by elemental analysis and NMR. 4-bromo allyl phenyl ether was synthesized by the reaction between 4-bromophenol and allyl bromide. Self assembled mono-layers of these materials have been covalently grafted onto (111) hydrogenated silicon surfaces through thermal hydrosilation with the alkene end by Si–C bonding mechanism. Monolayer formation was carried out using solutions of the alkene in the high boiling point solvent 1,3,5-triethylbenzene and was characterized by X-ray photoelectron spectroscopy (XPS), contact angle, Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). We anticipate these monolayers as potential dielectric materials for organic electronics © 2007 Published by Elsevier B.V.

Keywords: Allyl phenyl thiophene ether; Self assembly; Thin film

1. Introduction

Silicon, as a highly compatible microfabrication material for the mass production of integrated devices, is ideal for the fabrication of organic thin film field effect transistors [1–3]. The modification of silicon to form required interface is typically via silane chemistry on the oxidized silicon surface. However, silane chemistry is prone to multilayer formation and has limited stability in aqueous media [1]. Si–C linked monolayers formed by reaction of alkenes with Si–H terminated silicon surfaces provide an alternative self assembly system that is extremely robust, highly controllable, and well suited to the modification of silicon micro- and nanostructures [1,4–6]. There has been much recent interest in organic mono-layers covalently grafted onto atomically flat silicon surface through direct Si–C bonding as it has potential applications in many fields such as molecular electronics, sensor devices as well as template for biological recognition, etc. [7–10]. These self assembled mono-layers via Si–C bonding has no surface states in the gap and hence exhibit excellent electronic quality together with improved chemical resistance to aging in air or in aqueous media [7]. Linford et al. reported the hydrosilation of alkene on hydride terminated silicon, attained much attention with the discovery of the high density alkyl packing [9]. This passivates the surfaces from oxidation and can yield highly uniform self-assembled mono-layers on atomically flat Si(111). This is the first report of allyl phenyl thiophene ethers self assembled monolayers, covalently bound to atomically flat silicon surfaces capable of binding to organic semiconductors or other further surface modification. The higher homologues series are expected to show dielectric behavior.

2. Experiment

All chemicals are of high purity from Sigma-Aldrich/Fluka and used as received unless otherwise stated. \textsuperscript{1}H NMR was obtained in CDCl\textsubscript{3} solution unless otherwise indicated, and chemical shifts are reported in parts per million (ppm, δ) which

* Corresponding author.
E-mail address: ngsc@ntu.edu.sg (S.C. Ng).

0040-6090/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.tsf.2007.07.120
was taken on a BRUKER NMR spectrometers (300 MHz). Coupling constants are reported in hertz (Hz). Spectra splitting patterns are designated as s, singlet; br, broad; d, doublet; t, triplet; m, multiplet. For making the SAMs, 1,3,5-Triethylbenzene 1,3,5-Trimethylbenzene was redistilled from sodium under vacuum, and stored over molecular sieves under an argon atmosphere. All solvents were redistilled and stored in molecular sieves. Semiconductor-grade 30% H2O2 and 98% H2SO4 were used for cleaning Si–(111) wafer and 40% NH4F solution for etching.

Allyl alcohol was coupled with p-bromophenol to synthesize allyloxy bromophenol by following the published procedure [11]. This procedure completely eliminates the use of metallic sodium as mentioned in the versatile Williamson’s synthesis of ethers.

1-alloyloxy-4-bromo-benzene was synthesized by adding 1.1 equivalent of allyl bromide(1.27 mol, 110 ml) to a mixture of 4-bromophenol (1.16 mol, 200 g) and 1.3 equivalent K2CO3 (1.50 mol, 207 g), and the mixture was heated at 60 °C for 50 min. After cooling, the reaction mixture was poured into water, and extracted with Et2O. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous MgSO4, and concentrated under reduced pressure. The residue was purified by vacuum distillation to afford the final product. 1H NMR (300 MHz, CDCl3) δ 7.40 (d, J=9.1, 2 H), 6.84 (d, J=9.1 Hz, 2 H), 5.99–6.10 (m, 1 H), 5.46(dq, J=17.2, 1.6 Hz 1 H), 5.33 (dq, J=10.6, 1.4 Hz 1 H), 4.54 (dt J=5.1, 1.6 Hz, 2 H).

Allyl phenyl thiophene ether was synthesized by Grignard reaction between bromo alkenyl phenyl ether and 2-bromothiophene in anhydrous ether. 1H NMR (300 MHz, CDCl3) δ 7.36 (m, 2H), 7.25(d, J=7.8 Hz), 7.00(m 1 H) 6. 88(m, 1 H) 6. 75 (m, 2 H), 6.05–6.17 (m, 1 H), 5.50(d, J=1.6 Hz 1 H), 4.50 (m, 2 H).

The monolayers of alkenyloxy phenyl and alkenyloxy phenyl thiophene were prepared by the general method adopted by Gooding et al. [8]. Si (111) wafers were cleaved into pieces (approximately 15×15 mm2 ) and cleaned in concentrated H2SO4/30% H2O2 (3:1, v/v) at 90 °C for 20–30 min followed by copious rinsing with Milli-Q water. Hydrogen terminated Si (111) surfaces were prepared by etching in a deoxygenated 40% solution of NH4F for 15–20 min. [9]. The formation of

Fig. 1. Structure synthesized allyl phenyl thiophene molecules used as self assembled mono layers through Si–C bonding.

Fig. 2. XPS of monolayer of allyl phenyl thiophene ether formed by hydrosilation with Si–H. (a)wide spectrum (b) narrow scan of C1s showing formation of Si–C and C–O bonds (c) narrow scan of O 1s showing the peak arising mainly from ether oxygens of the organic monolayer at 532.6 eV (d) narrow scan of Sulfur showing peak at 63.9 eV.
monolayers was achieved via thermal reaction in a deoxygenated solution of the alkene in 1,3,5-triethylbenzene under an inert atmosphere at 200 °C for 2–6 h. After the reaction, the sample was rinsed several times with dichloromethane and ethyl acetate and blown dry under a stream of argon.

XPS measurements were carried in a Kratos AXIS spectrometer (UK) with the monochromatic Al K-alpha X-ray radiation at 1486.71 eV. The base vacuum in XPS analysis chamber was about 1×10^{-9} Torr. Contact angle measurements were determined using a Rame-Hart contact angle goniometer. The experimental uncertainty in the contact angle was estimated to be ±4°. Tapping mode AFM was used to characterize the sample flatness using Digital Instruments (Dimensions 3100, Nanoscope III a). In-situ STM scanning was done using a micro-droplet of a solution of allyl phenyl ether (∼ 0.05 mg/ml) in n-tetradecane (Aldrich, 99.99%) deposited on a freshly cleaved HOPG sample (10×10 mm²). STM imaging was performed at the n-tetradecane/HOPG interface using a Pico-SPM (Molecular Imaging) in a constant-current mode at room temperature.

3. Results and discussion

To create dense self assembled monolayers with sufficient robustness against molecular penetration, we have used specifically synthesized alkenyl ethers with an aromatic and thiophene end group. The chemical structure of the newly synthesized molecule is shown in Fig. 1. The SAMs are created in one step process without the need for chemical modification. After modification of the Si–H surface with the phenyloxy alkene, XPS was used to verify the composition of the monolayer and assess the quality of the sample. The XPS survey spectrum (Fig. 2a) showed the presence of carbon and oxygen as expected for the grafted monolayer in addition to the silicon peaks from the underlying substrate. The silicon 2p narrow scan did not show a significant peak between 102 and 105 eV characteristic of oxidized silicon, confirming the high quality of the sample. The carbon 1s envelope (Fig. 2b) was fitted with three peaks at 284.6 eV, 282.75 eV and 286.28 eV corresponding to the C–C, C–Si and C–O linked carbons. The oxygen 1s narrow scan (Fig. 2c) was dominated by the peak arising mainly from ether oxygen of allyloxy phenyl ether monolayer at 532.6 eV. Peak of oxygen associated with trace levels of oxidized silicon was not observed. The typical thiol peak for thiophene was observed at 163.9 eV.

Upon self assembly on a hydrogenated silicon surface, the π–π interaction between the phenoxy end groups of adjacent molecules creates an intermolecular top link, leading to a more closely packed surface. So monolayers formed with phenoxy end groups is expected not only show very low leakage current but also allow the use of pentacene as the organic semiconductor [12]. Of all organic semiconductors that have been used to prepare organic TFTs, small molecules such as pentacenes and oligothiophenes have shown by far best electrical performance, including carrier mobilities of 1 cm² V⁻¹ s⁻¹ and more [12–16]. Halik et al. [12] attempted to make pentacene TFTs on monolayer dielectrics with a linear end group (octadecyltrichlorosilane) and failed, presumably because the interaction between the pentacene and the CH₃-terminated SAM was so severe that the molecular ordering in the pentacene layer was insufficient to

![Figure 3. AFM image (2.2 μm x 2.2 μm) of alkenyl phenol ether self assembled on Si via Si–C bonding indicating monolayers to be molecularly flat over large area.](image)

![Figure 4. STM of allyl phenyl ether at the n-tetradecane/HOPG interface. A typical line profile of five rows is also shown.](image)

Fig. 3. AFM image (2.2 μm x 2.2 μm) of alkenyl phenol ether self assembled on Si via Si–C bonding indicating monolayers to be molecularly flat over large area.

Fig. 4. STM of allyl phenyl ether at the n-tetradecane/HOPG interface. A typical line profile of five rows is also shown.
support carrier transport. In this view monolayers formed with phenoxy and thiophene end groups have high potential for making organic thin film devices.

To understand the nature of the monolayer better, besides the detailed X-ray photoelectron spectroscopy discussed above, scanning probe microscopy including tapping mode atomic force microscopy (AFM) (Fig. 3) and scanning tunneling microscopy (STM) on highly oriented pyrolytic graphite (HOPG) was performed. Tapping mode AFM was used to characterize the sample flatness and density and to image the SAM defects. It was evident from the atomic force microscopic images that the monolayers were molecularly flat over very large areas. The roughness of the SAMs on Si was found to be 1.4 nm. The SAMs were free of defects and hence is suitable for device applications. Self assembly of molecules on HOPG were studied using STM. Typical scanning parameters were 0.1–0.2 V for the tip voltage and 0.11 nA for tunnelling current. Long range ordering of ally phenyl ether into regular rows of around 1.5 nm wide on HOPG was observed (Fig. 4). It also shows line profile of five such rows each. The STM images were free of domain boundaries (Fig. 4) and long range ordering was observed.

Thus, the self assembled monolayers formed is defect free and atomically flat over a large area and is composed of randomly oriented benzene rings. Such kind of arrangement allows the ordering of small organic molecules. In this way the presence of the synthesized molecules as insulating monolayer (dielectric) and pentacene as organic semiconductor may provide an efficient device performance due to a better matching of these materials in surface interface energy depending on the organic nature.

Upon self assembly, the static contact angle typically increased from 45° to 71° confirming the formation of densely packed SAMs. A device could be completed after depositing pentacene on the top of the monolayer and making source and drain by thermally evaporating gold through a shallow mask. The higher homologues series of such monolayers, we anticipate potential dielectric materials for organic electronics.

Acknowledgments

Funding from A*STAR Singapore (Project No 052 117 0032) is gratefully acknowledged.

References